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Study of 3-Ethylamino-but-2-enoic acid phenylamide as a new ligand for preconcentration of lanthanides from aqueous media by liquid-liquid extraction prior to ICP-MS analysis

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ABSTRACT

In the present work the potential of a new ligand 3-Ethylamino-but-2-enoic acid phenylamide (representing the class of enaminones) for selective preconcentration of lanthanides (La, Ce, Eu, Gd and Er) from aqueous medium is examined. Liquid-liquid extraction parameters, such as pH of the water phase, type and volume of organic solvent, quantity of ligand and reaction time are optimized on model solutions. Recovery of lanthanides by re-extraction with nitric acid makes the LLE procedure compatible with Inductively Coupled Plasma Mass Spectrometry. Spectral and non-spectral interferences are studied. Two isotopes per element are measured (with exception of La) for dynamic evaluation of the potential risk of spectral interference in variable real samples. The selectivity of complex formation reaction towards concomitant alkali and alkali-earth elements eliminates the interferences from sample matrix. Subjecting the standards to the optimized extraction procedure in combination with Re as internal standard is recommended as calibration strategy. The accuracy of developed method is approved by analysis of CRM Bush branches and leaves *(NCS DC 73348)* and recovery of spiked water and plant samples. The method's limits of detection for both studied objects are in the ranges from 0.2 (^{158}Gd) to 3.7 (^{139}La) ng l^{-1} and 0.02 (^{158}Gd) to 0.37(^{139}La) ng g^{-1} for waters and plants respectively. The studied compound is an effective new ligand for preconcentration/separation of lanthanides from aqueous medium by LLE and subsequent determination by ICP-MS.

1. Introduction

The increased scientific interest in determination of lanthanides (Ln) in environmental objects is related to the possibility of their usage for identification the geographic origin of different plants [1], assessment of the pollution risk associated with their increased application in superconductors production; monitoring the environmental impact of coal fly ash emitted by power plants [2] and the dust deposited on tree leaves [3,4]; investigation of soil-to-plant transfer factors and possibility for accumulation of certain lanthanides in plant-derived food products and agricultural crops [5,6]. Mechanisms of transmission, distribution and fractionation of lanthanides in the environment are not sufficiently explored [7]. Their biological toxicity is not well studied but the inhibition effect on the development of marine algae was recently verified [8]. It has been established that the similarity of certain properties of the lanthanides to those of biologically important metal ions (e.g. Ca^{2+}) can cause their replacement in biological tissues [9]. Therefore, it is necessary to develop sensitive and accurate analytical methods for monitoring trace levels of lanthanides in environmental objects with complex matrices.

Since Lanthanides are widely distributed at low levels in the environment, multi-elemental and highly sensitive analytical techniques such as: Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [3,4,9–19] (incl. Ultrasonic nebulization, isotope dilution SFMS [12], ETV [20,21] etc.); ICP-AES [2,22,23] and NAA [24]; are used for their determination.

Despite its undeniable advantages, ICP-MS suffers from some serious drawbacks in lanthanides determination. The presence of alkali and alkali earth elements in environmental samples in concentrations considerably higher than those of lanthanides (usually at levels of ng l^{-1} for water), can lead to severe spectral and non-spectral interferences, making the accurate determination of lanthanides problematic [4,8,13,24,25]. Variable matrix composition of plants, soils and sediments poses serious challenges to the accuracy of analytical methods for the determination of trace contents of lanthanides in real objects [15,26]. Although

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mathematical correction may be applied in some cases [3,13,24] the preliminary separation of analytes from sample matrix is a wide-spread approach for elimination or at least alleviation of matrix effect. Therefore, the development of reliable analytical methods for pre-concentration is important [27–29]. Diversity of methods for separation of lanthanides have been reported: liquid-liquid extraction (LLE) [16,30–33], dispersive liquid-liquid extraction (DLLME) [16,21], ion exchange techniques [4,15], cloud point extraction [34] or micelle mediated extraction [22], ionic liquids [35], solid phase extraction [6,14,17,19,23,36] and solid phase extraction with nanomaterials, such as: TiO_2[19] or modified magnetic nanocomposites [13,23]. Moreover these procedures allow pre-concentration of the analytes, leading to improvements in the limits of quantification [13,16].

In their review on preconcentration of lanthanides Rao and Kala [27] emphasize that most of these methods are based on chemical reaction between target ions and different ligands, or active functional groups bonded on the sorbent surface. Solvent extraction is a classical method for separation/ preconcentration. Among the main weaknesses of this method are: mutual solubility of both phases at higher volume ratios, formation of emulsions as well as the low tolerance of ICP towards organic solvents which requires re-extraction of analytes in aqueous media. Nevertheless LLE of lanthanides is widely used in trace analysis because of its simplicity, ease of performance and well known principles [30,31,35]. Common ligands for LLE of lanthanides are variety of organophosphorus compounds [17,20,30,35], 1-Phenyl-3-Methyl-4-Benzoyl-5-Pyrazolone [20,31] and classical reagents as 8-hydroxyquinoline [32,33].

The main drawbacks of phosphorus-containing compounds are their toxicity and increased risk of spectral interferences caused by polyatomic ions of phosphorus. The lack of selectivity of 8-hydroxyquinoline, which is capable of forming stable complexes with most metal ions, may cause problems with co-extracted elements which are in significantly higher concentrations in the environmental objects than the lanthanides.

In the present study the potential of a new ligand (representing the class of enaminones) for selective separation and preconcentration of lanthanides from aqueous solutions of environmental samples was examined.

Compounds incorporating conjugated system N–C=C–C=O in their structure are called beta-enaminones and can be subdivided into beta-enaminoketones, beta-enaminoesters and beta-enaminoamides. We were attracted to this class of compounds because of their potential to form chelate complexes with various metal ions. Several researchers have published studies on the potential of enaminone compounds to form stable complexes with lanthanide ions. Reaction between enaminones and lanthanides was first reported in [37], wherein the authors synthesized Ln derivatives enaminones, insoluble in typical organic solvents, because of their polymeric structure. Studying the calixarene activity towards lanthanides the authors of [38] have reported about the synthesis of stable complexes. Authors surprisingly discovered that in the obtained complexes Ln are bonded to the enaminone part of the studied compound. Recently Chopin et al. [39] reported the successful synthesis and characterization of novel nonanuclear complexes of Cu(II)–Dy(III) with trifluoromethyl-substituted enaminone ligands. The three Dy(III) ions included in the complex structure exhibit eight-coordinated pattern by the oxygen atoms (from bridging OH^- groups, alkoxy groups of the ligand and coordinated water). The resulting poly-nuclear architecture shows interesting magnetic properties – it acts as a Single-Molecule Magnet (SMM).

Our initial investigations on the complexation activity of two compounds from the class of enaminones, showed their promising efficiency towards lanthanide ions [40]. This motivated the systematic study on the applicability of new compound i.e. 3-Ethylamino-but-2-enoic acid phenylamide as a ligand for separation/preconcentration of lanthanide ions by LLE followed by their ICP-MS determination in environmental samples.

The studied compound is more environmentally benign in comparison to the traditionally used ligands as alkyl/phenyl phosphates. Our expectations were to obtain improved selectivity and to avoid reagent-related spectral interferences, because the elemental composition of the studied compound is identical to the water-loaded plasma itself.

To the best of our knowledge there are no previous investigations related to the use of enaminones as reagents for separation/ preconcentration of lanthanide ions prior to their determination by spectral methods.

2. Experimental

2.1. Instrumentation

An ICP-MS Agilent 7700 (Tokyo, Japan) was used for determination of lanthanides concentrations in all sample solutions. Operating conditions and measured isotopes are summarized on Table 1. Microwave digestion system - MDS-81D, CEM Corporation, (Indian Trail, NC, USA) was used for plants mineralization according to digestion procedure given in Section 2.4.

2.2. Reagents

All reagents and solvents were analytical grade and used without further purification. Doubly distilled water were used for preparation of all solutions. Monoelemental solutions of Ce, Er, Eu (1000 mg l^{-1}), Zr, Rh (100 mg l^{-1}), Pt, Pd (50 mg l^{-1}), were purchased from CPA-spectr™ and used after dilution. Rhenium (10,000 mg l^{-1}) was obtained from Merck, Darmstadt, Germany. Calibration solutions for La and Gd were prepared by dissolving appropriate amount of Gd_2O_3 (99,9%, Sigma-Aldrich) and La $(NO_3)_3 \cdot 6H_2O$ (99,99%, trace metals basis, Sigma-Aldrich) in 1 mol $l^{-1}$$HNO_3$ on heating plate and then diluting to the final volume with double distilled water. Both stock solutions were prepared with concentration 1000 mg l^{-1}. NH_4NO_3/NH_4OH buffer solution with pH=8,3 was prepared from NH_4OH and NH_4NO_3 (Merck). Re-extraction is done with diluted nitric acid purchased from Merck. Studied ligand (3-Ethylamino-but-2-enoic acid phenylamide, (Fig. 1) was synthesized according to a procedure

Table 1
ICP-MS working conditions.

Plasma conditions	
RF Power	1.5 kW
Plasma gas - Ar	15 l min^{-1}
Nebulizer	Micromist (glass expansion)
Auxiliary gas flow rate	0.9 l min^{-1}
Spray chamber	Scott double pass
Interface cones	Ni
Pump speed	0.2 rpm
Mass spectrometer	
Resolution	0.65 amu
Measurement mode	Peak hoping
Replicates	5
Points per peak	1
Acquisition time	0.1 s
Measured isotopes	^{89}Y,^{103}Rh,^{105}Pd,^{139}La,$^{140,\ 142}Ce$,^{151,} ^{153}Eu,$^{157,158}Gd$,$^{166,168}Er$,^{143}Nd,^{185}Re,^{195}Pt

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